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Effects of temperature on the mechano luminescence of gold-doped ZnS phosphors

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Abstract : The present paper reports the effects of temperature on the mechanoluminescence (ML) intensity of gold-doped ZnS phosphors. The ML intensity decreases with temperature and follows the relation $I_t = I_t^0(1-T/T_c)^n$ the value of n lies between 0.90 and 1.10 for ZnS phosphors. Generally, ML of ZnS phosphors ceases much below their melting point. The process of thermal quenching in the ML can be understood by electro and photoluminescence (PL) studies. The faster rate of decrease of ML intensity than the PL intensity suggests that in addition to increase in the non-radiative transition probability, the temperature also affects some other parameters such as piezoelectric constant or surface charge density responsible for the ML excitation.

Keywords : Mechanoluminescence (ML), electroluminescence (EL), photoluminescence (PL)

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1. Introduction

The luminescence produced during mechanical deformation of solids is known as mechanoluminescence (ML) or triboluminescence. The ML links the mechanical, spectroscopic, electrical, structural and other properties of solids. The dependence of luminescence intensity on temperature is extremely interesting from theoretical and experimental points of view. Although much attention has been paid to many aspects of the luminescence in the solids, the influence of temperature has been least understood to date. Many workers have studied the effect of temperature on the ML of crystals. Some investigators [1-3] have measured the effect of temperature on the ML of certain crystals and have found that the ML intensity decreases with the increasing temperature. Longchambon [4] and Stranski *et al* [5] have concluded that the recombination of atoms or ions is the primary reason for the decrease of ML intensity with increasing temperature of the substance. Wick [6] has reported the emission of light at the instant when there is a sudden change in the temperature of the crystals.

Our main interest is to understand the mechanism of ML excitation in gold doped ZnS phosphors. For this purpose, it was anticipated that the temperature dependence of ML of phosphor might provide some meaningful indication. Furthermore, as the temperature dependence of ML is of complex nature, an attempt has been made also to measure the temperature dependence of the electro and photoluminescence of the gold-doped ZnS phosphors.

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2. Experimental

The phosphors were prepared following the conventional technique [7-10]. The ZnS: Au, Cl (Cubic) and ZnS: Au, Cl (Hexagonal), phosphors were prepared by firing for one hour in nitrogen atmosphere at 900°C and 1100°C respectively. After the required firing time, the phosphors were slowly cooled at a rate of 50°C per hour. The activator concentration in gold-doped cubic and hexagonal ZnS phosphors was taken to be 300 ppm as these phosphors show optimum ML for this concentration. For each set of the measurement, 5 mg of the phosphor was placed on the transparent lucite plate which was used as base for crushing the phosphors. An RCA 931 photomultiplier tube was used for monitoring the luminescence from below the lucite plate. The ML was excited impulsively by dropping a hollow cylinder of 800 gm (2 cm diameter) from a fixed height of 40 cm. The ML measurements were carried out by the method described earlier when the system had attained a steady state temperature [11].

For measuring the effect of temperature on the ML of phosphors, the phosphors were heated by using two heating filaments fixed close to lucite plate and the filaments were connected to a variac. By changing the voltage supplied by variac, the phosphors could be heated to any desired temperature. The temperature range studied was from room temperature to 330°C. Because of this, the copper-constantan thermocouple used to measure directly the temperature of phosphor, could be taken out before the deformation of the crystal. To avoid the heating of the photomultiplier tube, a thick rubber sheet with a hole at its center was placed between the lucite plate and photomultiplier housing.

For studying the effect of temperature on the EL of phosphor, two heating filaments of 65 watts were placed between an asbestos sheet and a polished aluminium plate. The phosphors were fixed onto the aluminium plate using toluene. The aluminium and thereby phosphors could be heated to any desired temperature by connecting the heating filament to a variac. The PL was excited by the light passing through a 365 nm (UV) filter placed between tungsten halogen lamp and the phosphor. The light coming out of the phosphor falls onto the entrance slit of a grating monochromator Model HM-104 supplied by Central Electronics Ltd Sahibabad. The RCA 6193 photomultiplier tube connected to a digital picoammeter, was placed near the exit slit of the grating monochromator for measuring the PL intensity at different temperatures.

3. Results

Figure 1 shows the kinetics of ML for different temperature. Figures 2 and 3 show the effects of temperature on the ML and PL intensities of ZnS: Au, Cl (Cubic) and ZnS: Au, Cl (Hex.) phosphors respectively.

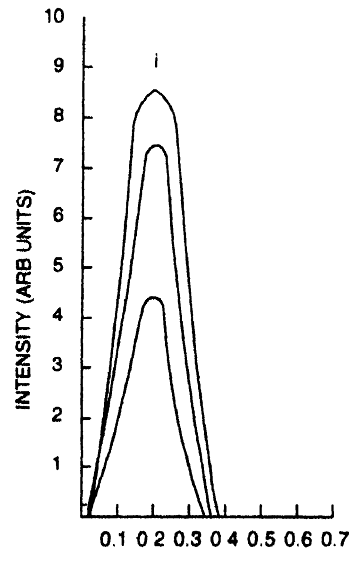

Figure 1. Time dependence of the ML intensity of ZnS. Au, Cl(Hex) phosphors for different temperatures.

Figures 4 and 5 show the effects of temperature on the EL brightness of cubic and hexagonal ZnS: Au,Cl phosphors. It is found that the ML, EL and PL disappear beyond a particular

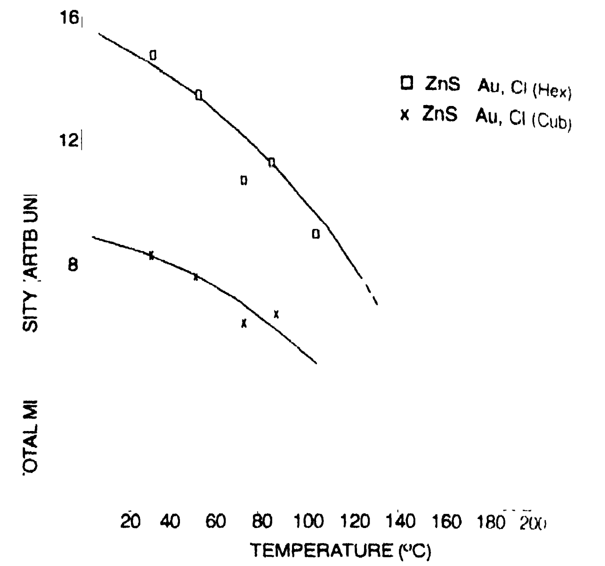

Figure 2. Effect of temperature on the total ML intensity of the ZnS: Au, Cl(Hex) and ZnS Au, Cl(Cubic) phosphors

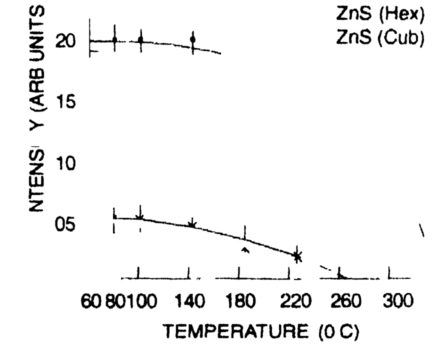

Figure 3. Effect of temperature on the PL intensity of ZnS Au Cl (Hex) and ZnS: Au, Cl (Cubic) phosphors.

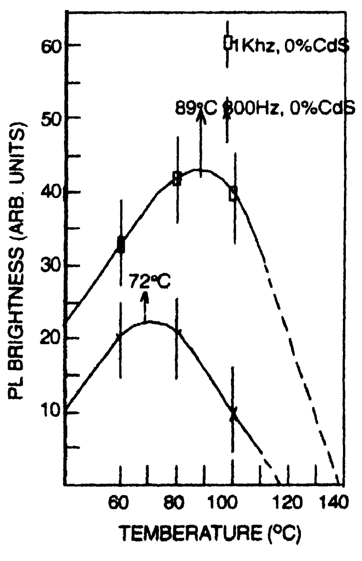

Figure 4. Effect of temperature on the EL brightness of ZnS Au, Cl (Cub) phosphors.

temperature. Generally, the temperature at which ML disappears is in the range comparable to the temperature at which EL and PL disappears. The critical temperature at which ML, EL and PL disappear in ZnS: Au, Cl (Cubic) and ZnS: Au, Cl (Hex.)

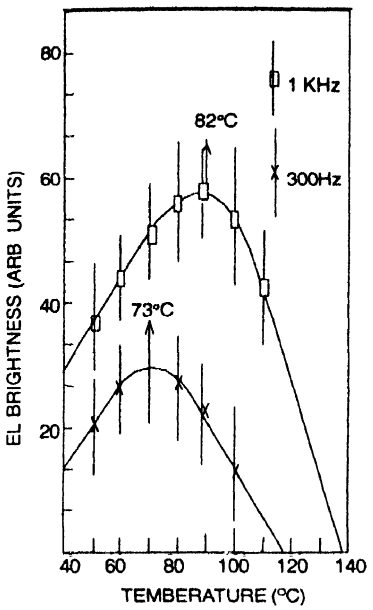

Figure 5. Effect of temperature on EL brightness of ZnS. Au, Cl (Hex) phosphors

phosphors are shown in Table 1. It is to be noticed that initially, the EL brightness increases with temperature, attains a maximum value and then finally decreases with temperature. The peak corresponding to EL brightness *versus* temperature curve shifts towards higher temperature values with increasing frequency of the applied voltage used for exciting the EL.

Table 1. Critical temperatures (extrapolated) at which ML, EL and PL disappear in the phosphors.

Phosphor	Critical temperature		
	For ML (°C)	For PL (°C)	For EL (°C) (1KHz, 650V)
ZnS Au, Cl(Cubic)	155	262	129
ZnS Au, Cl (Hex)	165	326	133

For studying the effect of temperature on the ML of phosphors, the phosphors were kept on the lucite plate in the steady state. The time of annealing at this temperature, does not have any considerable effect on the ML intensity of the phosphors. Figure 6 shows that the plot of log I_T *versus* log $(1 - T/T_c)$ is a straight line with a positive slope. The value of the slope lies between 0.90 and 1.10. Thus, the decrease of ML intensity with temperature follows the relation

$$I_T = I_T^0\left(1-(T/T_c)\right)^n, \tag{1}$$

where I_T^0 is a constant, n is the slope of log I_T *versus* $(1 - T/T_c)$ plot and T_c is the temperature at which ML disappears.

4. Discussion

As the ML in phosphors is excited impulsively, fracture of crystallites is primarily responsible for the ML emission. The

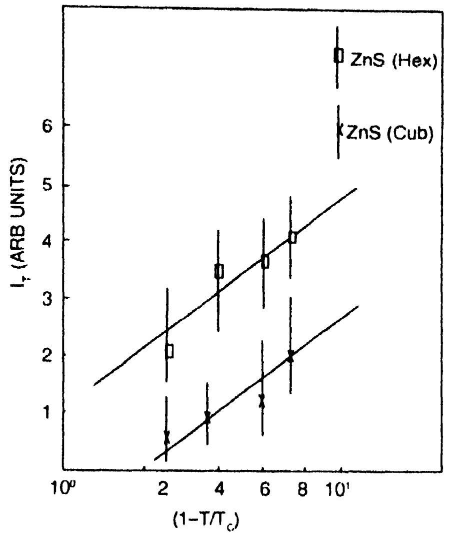

Figure 6. Plot of log I_T *versus* $(1 - T/T_c)$ for different ZnS Au, Cl (Hex) and ZnS Au Cl (Cubic) phosphors

ML intensity in phosphors will depend strongly on the charge density and the charge distribution on the fracture surfaces near the crack tip. For the decrease in the ML intensity of phosphors, the following facts may be responsible:

(i) Considerably less fracture surface is being created at high temperature.

(ii) The charge density is not reaching the same values during fracture as at lower temperature, and

(iii) The charge is more rapidly leaking off the fracture surface due to increase in the conductivity at higher temperature.

Since the ML excitation takes place instantaneously with the creation of new surface, the first two factors may be more responsible for the temperature effect in ML than the third one.

Chandra *et al* [12] have reported that the ML activity of piezoelectric crystals ceases completely near their melting point. This may be due to the absence of ruptured bonds and the disappearance of piezoelectricity near the melting point. For the crystals whose structure changes before the melting point, a different type of the temperature effect on the ML is expected [13]. As the probability of the ML excitation depends on many physical properties of the phosphors such as piezoelectric constants, fracture stress, charge leakage, rate of radiative recombination *etc*, no quantitative approach for the effect of temperature on the ML phosphors is still reported.

It has been observed that the ML intensity of the phosphors decreases more rapidly than the PL intensity with rise of temperature. This fact shows that in addition to the luminescence efficiency, some other factors depending upon structural parameters responsible for the ML excitation also change with temperature of the phosphors.

The disappearance of ML of the phosphors at temperatures much below their melting points, suggests that at these temperatures the area of newly created surfaces should not change considerably. This fact shows that the decrease in the ML activity of phosphors with increasing temperature should be related to the decrease in the charge density of the newly created surfaces.

It is known that the decrease of ML intensity with temperature of the phosphor follows the relation $I_T = I_T^0(1 - T/T_c)^n$ where T_c is the temperature at which ML disappears. The value of n lies between 0.90 and 1.10 for the phosphors chosen in the present investigation. The value of n has been found to be 0.50 for LiF, NaF and NaCl crystals, where the decrease of surface charge with temperature is only responsible for the decrease of ML [14]. The higher value of n for the phosphors suggests that both the mechanically induced electric field and the luminescence efficiency should be responsible for the temperature dependence of ML of phosphors.

The decrease of PL efficiency with temperature is due to the increase in the probability of non-radiative transition [9]. The faster decrease of ML intensity with temperature as compared to that of PL, suggests that in addition to increase in the probability of non-radiative transition, some other parameters like piezoelectric constant or surface charge density that decrease with temperature, cause the faster decrease in ML efficiency.

It has been mentioned that the EL brightness is maximum for a particular temperature of the phosphors and the temperature related to the peak of the EL intensity *versus* temperature curve shifts towards higher values with increasing frequency of the applied electric field. At low temperature, the electrons captured in traps in the low field region, have relatively lower chance of escape and therefore, the number of electrons in the available frequency interval increases and hence, the brightness falls down because of the thermal quenching [15]. Thus, with rise in temperature, the brightness increases slowly, attains a maximum value and then falls down.

With increase in the field frequency, the brightness peak shifts towards higher values of the temperature. The reason is that due to increase in frequency, the available time for the excitation of the trapped electrons is decreased and therefore higher thermal energy is required to get these traps emptied within the limited time interval.

It is quite evident from the temperature-dependence curve that the EL is more affected by the existence of traps as compared to PL. It seems that in EL process, the electrons from traps or (shallow) donors from the barrier region are responsible for the emission; however in the PL process, the valence band electrons rather than traps are more responsible for the emission

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